Characterization of red gypsum as a potential feedstock for mineral carbon dioxide sequestration

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Abstract—Red gypsum, a by-product from titanium dioxide manufacturing industry is a potential raw material for mineral carbon dioxide sequestration application. In this study, the physical and chemical characteristics of red gypsum were analyzed using X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Brunauer-Emmett-Teller (BET) methods. The experimental results showed that red gypsum possesses high content of calcium and iron that makes it a potential feedstock for mineral carbonation experiments.

Keywords- Red gypsum; Titanium dioxide; CCS; Mineral carbon dioxide sequestration

I. INTRODUCTION

Industrial by-products are produced from industrial activities such as manufacturing, production and construction. These industrial wastes must be properly managed in order to reduce the risk towards health and environment as they are toxic, ignitable, reactive and corrosive in nature. Some of these hazardous wastes even end up in landfills [1]. Red gypsum is one of the most important industrial wastes that was produced from titanium dioxide manufacturing using Ilmenite as raw material [2].

Ilmenite which contains approximately 43-65% titanium dioxide (TiO2) was widely used as raw material for titanium dioxide manufacture. Titanium dioxide is extracted from ilmenite through a stepwised processes [3]. The first step is the chemical reaction of ilmenite with sulphuric acid to digest the ore. In this process, the titanyl sulphate (TiOSO4) and iron sulphate (FeSO4) is produced. The second step is the clarification of produced liquor through solid separation. This is followed by the hydrolyzation of the liquor by steam for TiO2 precipitation. Finally the hydrated TiO2 is separated and washed with water to remove the impurities [4]. Fig. 1 shows the processes used in the Huelva factory for TiO2 production. The neutralization of the spent sulphuric acid during TiO2 extraction with limestone and lime produces a by-product named red gypsum (CaSO4·2H2O). In the next step, the red gypsum is filtered and separated from water and the produced water is recycled in the process. Equation (1) shows the chemical reaction of red gypsum production.

\[ \text{Ca(OH)}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \]  

The titanium dioxide industry in Malaysia produce 400,000 tonnes of red gypsum annually that could be utilize for CO2 sequestration. Globally, 75% of CO2 emitted into atmosphere are mostly contributed by the consumption of fossil fuels [5]. At present, fossil fuels supply more than 86% of the world energy requirement. Over dependence on fossil fuels have resulted in an increase in the CO2 concentration from 280 ppm in the 1750s to 389 ppm in 2010 [6,7]. As a result an increase of global temperature by 1.8 to 4°C has been predicted by 2100 because of the increase in atmospheric CO2 concentration [8]. Fig. 2 shows the scenarios relating the atmospheric CO2 concentration, CO2 emission, SO2 emission, temperature changes, and rising sea level [9].

Reducing the energy intensity, switching to non–fossil fuels, and enhancing CO2 sequestration by developing technologies to capture and sequester more CO2 are the available and applicable methods of reducing the atmospheric CO2 concentration. However, carbon capture and storage methods (CCS) are more preferred than the other methods [10]. The contribution of up to 15–55% of the cumulative global climate change mitigation effort by 2100 has been predicted by employing the CCS methods [11].

Mineral carbon dioxide sequestration is an exothermic chemical reaction between a metal oxide such as calcium, magnesium, or iron with CO2 to produce carbonates. This method mimics the natural rock weathering that takes place over geological time scale [8]. The energy state of the CO2 is about 400 KJ/mol and the energy state of the carbonate is between 60 to 180 KJ/mol. Therefore, the produced carbonates are thermodynamically stable, permanent, and environmentally benign. Furthermore this method is viewed as a leak-free CO2 disposal without the need for pre and post site monitoring [12].

Figure 1. TiO2 production scheme used in Huelva factory [4]
Calcium and magnesium are the most favorable mineral for mineral carbonation process. However they usually appear in the form of silicates due to their high reactivity [13]. In general, calcium and magnesium sources can be categorized derived from natural minerals and industrial by-products. Olivine (Mg$_2$SiO$_4$), wollastonite (CaSiO$_3$), and serpentine (Mg$_2$Si$_2$O$_5$(OH)$_4$) are the most widely used natural minerals for mineralization purposes [13,14]. Besides these natural minerals, industrial solid residues and wastes rich in magnesium and calcium are also potential sources for the mineral carbonation experiments [15-17]. The main advantages of using these industrial wastes include their availability in large quantity, lower cost, and the possibility of utilizing a waste stream [18].

The focus of the present work is on physico-chemical characterization of red gypsum, a by-product from titanium dioxide industry. The red gypsum is rich in calcium and is a potential raw material for mineral carbon dioxide sequestration.

II. MATERIAL AND METHODS

A. Material

The samples of red gypsum for this study have been collected from titanium dioxide industry in Terengganu, Malaysia. The samples were dried in an oven overnight at 45 °C to avoid any loss of their hydrated water.

B. Methods

In this study, detailed physical and chemical characterizations of red gypsum were performed. The XRD was used to find the mineralogical characteristics of the red gypsum. Major trace elements present were analyzed using aqua regia technique after the sample preparation. The major elements have been investigated using XRF. The SEM technique was used to study the morphology and the microstructure of the red gypsum. Thermogravimetric analysis (TGA) was used to measure the flow. BET was also used for particle size distribution measurements.

A. X-ray fluorescence (XRF)

The XRF analysis were carried out using a PW 1410 XRF Philip model with chromium target, PE crystal analyzer. The detector is coupled to a recorder to produce the XRF spectrum of the sample. Fig. 3 presents the spectrum of the red gypsum sample. The spectrum shows the major elements found in the sample and the height of each element represents the intensity of the particular elemental component. As shown in this figure, three major peaks were detected and identified as Ca, Fe, and S indicating that these are the major constituents of the red gypsum. The main elements of the red gypsum identified from the XRF analysis are presented in Table I. The XRF result shows that the red gypsum is mainly consist of CaO, Fe$_2$O$_3$ and SO$_2$ together with some insignificant impurities. Clearly, the red gypsum is rich with Ca, one of the most favorable minerals for mineral carbonation experiment and hence red gypsum could be a potential feedstock for the carbonation purposes. On the other hand, the carbonation of Fe could also be investigated for carbonation experiment given its content in the red gypsum.

B. X-ray diffraction

The XRD analysis was carried out with the speed of 1°C/min. Fig. 4 shows the XRD results in which the peaks of the red gypsum were detected at 0.541 and 0.217 nm. The XRD results showed that red gypsum, an industrial by-product could be a potential source of calcium and iron suitable for mineral carbon dioxide sequestration.

![Figure 2. Atmospheric CO$_2$ concentrations as observed at Mauna Loa from 1958 to 2008 (black dashed line) and projected under the 6 SRES marker and illustrative scenarios [9]](image)

![Figure 3. XRF spectrum of red gypsum](image)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>CaO</th>
<th>SO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>MnO</th>
<th>TiO$_2$</th>
<th>Au$_2$O$_3$</th>
<th>V$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. (%)</td>
<td>32.2</td>
<td>31.6</td>
<td>28.99</td>
<td>0.41</td>
<td>5.64</td>
<td>0.39</td>
<td>0.22</td>
</tr>
</tbody>
</table>
C. Aqua regia method

Table II shows the major elemental analysis of red gypsum using aqua regia method. Application of a natural mineral or industrial by-product in carbonation experiment requires the availability of calcium, magnesium and iron in its compositions. The results show that red gypsum has high calcium and iron content, confirming the findings from analyses using XRF and XRD. Therefore, it is possible to use red gypsum as raw material for mineral carbon dioxide sequestration purposes.

![Figure 4. X-ray diffraction of red gypsum](image)

![Figure 7. TGA analysis of red gypsum](image)

**TABLE II. ELEMENTAL CONTENT OF RED GYPSUM FROM AQUA REGIA**

<table>
<thead>
<tr>
<th>Comp</th>
<th>Ca</th>
<th>Fe</th>
<th>S</th>
<th>Mn</th>
<th>Mg</th>
<th>K</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. (%)</td>
<td>19.43</td>
<td>9.81</td>
<td>4.97</td>
<td>0.45</td>
<td>0.21</td>
<td>0.15</td>
<td>0.09</td>
</tr>
</tbody>
</table>

![Figure 5. Particle size distribution of red gypsum using BET analysis](image)

![Figure 6. Surface morphology of red gypsum as analysed by SEM](image)

D. Particle size distribution

Particle size distribution was measured using BET analyzer. Two samples of red gypsum were prepared and then analyzed with BET. Both samples were analyzed and the results are shown in Fig. 5. It was found that the average particle size of the red gypsum was between 50-100 micron, whereby the highest particle size concentration was identified at 70 micron. It is therefore confirmed that the red gypsum consisted of a fine grained material, suitable for utilization as the feedstock for carbonation experiment.

E. Scanning electron microscopy (SEM)

The SEM analysis was used to elucidate the microstructure and morphology of red gypsum. SEM results show that the red gypsum has tubular and prismatic crystal in its structure which makes the material a very favorable feedstock for mineral carbon dioxide sequestration. Analysis showed that red gypsum can be transformed into calcite with a poorly developed rectangular or rhombohedral shape and spindle-shaped vaterite [19]. Fig. 6 shows the results of SEM for red gypsum.

F. Thermogravimetric analysis (TGA)

Fig. 7 shows the weight loss of red gypsum as a function of temperature under nitrogen environment. Initially 20 mg of red gypsum was used and only 16.98 mg was left over after the experiment. The TGA result shows that dehydration occurs at temperatures around 100-160 °C. Beyond this temperature, no further significant weight loss was observed. It is most likely that any weight loss observed at 600-850 °C is related to that of CaCO₃ due to the emission of CO₂. Therefore, for future analysis of produced calcium carbonate there would be no confusion since raw gypsum did not give any peak at 600-850 °C and any produced peak is due to CO₂ emission from CaCO₃.

IV. CONCLUSIONS

The chemical and physical characteristics of red gypsum, a by-product of titanium dioxide manufacture were investigated in detail. Chemically, all analytical results proved that the red gypsum contains high concentration of calcium and iron, two important minerals for carbonation reaction. In addition, the physical analyses indicate that the material possesses narrow
particle size distribution and uniform tubular and prismatic surface morphology. These attributes positioned the red gypsum as a potential candidate for mineral carbon dioxide sequestration application.

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